

Study on the Preparation of Montmorillonite-Type Multiple Network Composite Gel for Coal Spontaneous Combustion and Its Firefighting Mechanism

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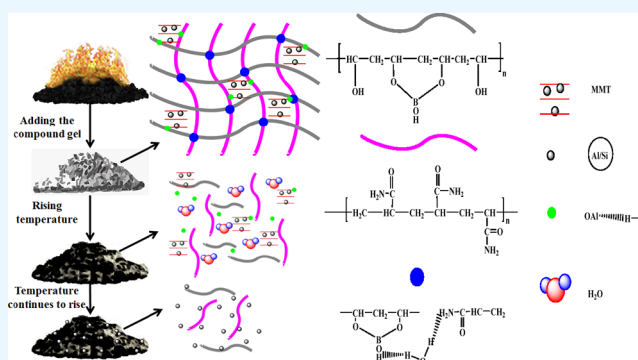
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ABSTRACT: This paper proposes a new montmorillonite-type multiple network composite gel for the prevention of coal spontaneous combustion. The first network is formed by the cross-linking of polyvinyl alcohol (PVA) and boric acid under alkaline conditions. The second network is formed as a result of intermolecular hydrogen-bonding interactions between polyacrylamide (PAM) and polyvinyl alcohol. Montmorillonite (MMT) is designed as the backbone material in the preparation of composite gels. The optimal ratios of the reactants of the composite gel were determined through orthogonal experiments. The experimental results showed that PVA had the greatest influence on the gelation time, whereas the PAM concentration had the strongest influence on the gel permeability. The optimal blending ratio was 4% MMT + 2.5% PVA + 1.5% PAM. The chemical performances of the composite colloids, such as inhibition rate, reactive functional groups, and kinetics, were investigated. Results showed that multiple network composite gels could effectively inhibit the coal spontaneous combustion reaction. Based on the principle of coal spontaneous combustion and the cross-linking network structure of the composite gel, the flame-retardant and fire-extinguishing mechanisms were also explored in terms of both physical and chemical inhibition pathways.



1. INTRODUCTION

China is among the world's largest energy producers, consumers, and carbon emitters.¹ CO₂ generated by the spontaneous combustion of coal accounts for more than 3% of total CO₂ emissions, and a large amount of CO₂ from coalfield fires is released into the atmosphere.^{2–4} To achieve the goal of carbon peaking and carbon neutrality at the earliest, it is imperative to prevent the risk of automatic coal combustion and reduce natural coal fires. Therefore, exploration of technologies to prevent and control the spontaneous combustion of coal has been one of the topics pursued by scientific and technical researchers.^{5–8}

To tackle the disasters of coal spontaneous combustion in a better manner, scholars and technicians have explored and implemented various intuitive methods of prevention of coal combustion, both at home and abroad. Among them, the use of advanced firefighting material is a promising and effective way to prevent coal spontaneous combustion, and scholars across the world have been developing different types of materials to control this hazard.^{9–12} Zhou et al.¹³ developed the three-phase foam which was composed of a non-combustible material (ash fly or mud), inert gas (nitrogen), and water for fire control. Xue et al.¹⁴ proposed a gel foam

using a composite foaming agent, modified polyethoxy silicone, water glass, and coagulant. Wang et al.¹⁵ prepared a novel biomass composite thermoresponsive gel produced by mixing konjac glucomannan (KGM) with fly ash (FA) to prevent coal spontaneous combustion. Huang et al.¹⁶ used sodium silicate as the base material and polyacrylamide as an additive to synthesize a composite gel that uniformly covered the coal surface and effectively blocked and inhibited the oxidation of coal. Dong et al.¹⁷ studied the effect of foam gel on the prevention and control of coal combustion in mining areas and found that the gel had better permeability and fluidity, and the foam formed a barrier on the surface of the coal body to hinder the release of harmful gases. Hu et al.¹⁸ proposed an anionic polyacrylamide (HPAM)–aluminum citrate gel system for the self-heating and spontaneous combustion of coal, which was found to be effective in controlling the gel formation time and

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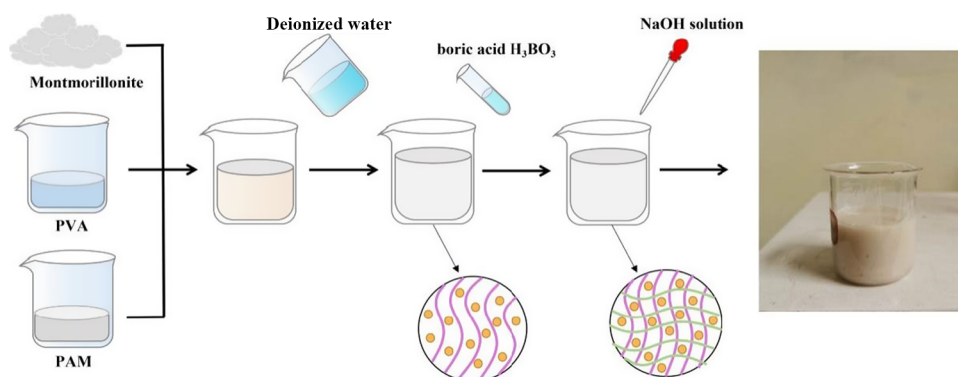


Figure 1. Schematic diagram of product preparation.

formed a gel barrier in the area of self-heating or gas leakage on the coal body, thus preventing the contact of air with the coal body. However, most of the gel materials have shortcomings in terms of poor structural stability, susceptibility to water loss and cracking, and decomposition by heat and cannot function on the coal body for a longer time.^{19–21} Moreover, fire prevention and control effect are poor and can even cause reignition of coal mine fire.

The colloidal structure determines the stability and fire-fighting ability of colloidal materials, and it plays an important role in the prevention of fire. The design of most of the firefighting materials currently available involves a single network structure, but the structural characteristics of the material are ignored, resulting in poor stability and durability during application. A single-network gel having a range of spatial structures of high-molecular-weight polymers is formed by the cross-linking of monomers through either single physical or chemical bonds. This kind of gel has some disadvantages, such as low cross-linking strength and poor mechanical properties. The gel with multiple networks provides new ideas for solving such problems, which can combine all the advantages of the two gel networks and improve the gel structure and its performance.²²

In this paper, the synthesis of the PVA/PAM/MMT multiple network composite gel from polyvinyl alcohol (PVA), polyacrylamide (PAM), and MMT has been proposed. The first network was formed as a result of cross-linking of polyvinyl alcohol and boric acid under alkaline conditions. The second network was formed due to the intermolecular hydrogen bonding between polyacrylamide and polyvinyl alcohol, whereas MMT served as the backbone material in the composite gels. The optimal ratio of the composite gel was determined through orthogonal experiments. The chemical performances of the composite colloid were also determined in terms of its inhibition rate, reactive functional groups, and the kinetic parameters. Based on the principle of coal spontaneous combustion and the cross-linking network structure of the composite gel, the flame-retardant and fire-extinguishing mechanisms were also explored in terms of both physical and chemical inhibition pathways. Moreover, this research also provides new ideas for solving the problem of coal spontaneous combustion in goaf caused due to the fully mechanized technology for top coal caving mining and enriches the technical means of fire prevention.

2. EXPERIMENTAL SECTION

2.1. Colloidal Materials and Preparation. Montmorillonite (MMT, $[(\text{Si},\text{Al})_4\text{O}_{10}]^{2-} \cdot n\text{H}_2\text{O}$) and polyacrylamide (PAM, $(\text{C}_3\text{H}_5\text{NO})_n$) were procured from Shanghai Aladdin Biochemical Technology Co., Ltd. Polyvinyl alcohol (PVA, $(\text{C}_2\text{H}_4\text{O})_n$), boric acid, calcium chloride, and sodium hydroxide were purchased from Shanghai Sinopharm Group Chemical Reagent Co., Ltd.

Certain amounts of montmorillonite, polyacrylamide, and polyvinyl alcohol were mixed in a dry beaker, and deionized water was slowly added to the beaker and stirred with a glass rod to reduce agglomeration. Then, this mixture was placed on a magnetic stirrer and well-stirred. Boric acid solution (1%, 10 mL) was added to the reaction mixture and stirred well. Further, 2% sodium hydroxide solution was added dropwise to the resulting solution, and the stirring was stopped when the pH of the solution reached about 9. It was allowed to stand until a complex colloid was formed (Figure 1).

2.2. Physical Properties of Gels. **2.2.1. Measurement of the Gel Formation Time.** Gelling time refers to the time required to transform a cross-linked system from a flowing liquid state to a solid gel with specific stability and strength after its formation. The gelling time should be controlled according to the firefighting process, mine conditions, and other practical factors. For extinguishing high-temperature fires or filling of leaks, the gelling time is maintained between 0.5 and 3 min. For blocking the spontaneous combustion of floating coal in the mining area, the gelling time is maintained to less than 10 min.

In this study, the time for gel formation was expressed using the trickle timing method. The time required for the prepared mixture to flow through the funnel into another beaker is recorded. The mixture in the cup was poured back through the funnel into another container, and the time taken was recorded. The above steps were repeated until the funnel drip time exceeded the last one by more than 50%. The last funnel drip time was noted as the gelling time.

2.2.2. Permeability Determination Experiments. The gel not only wraps the coal body when applied but also penetrates the pores of the coal body. Thus, it fills the pores and plays the role of oxygen barrier and plugging. Therefore, it is necessary to study the permeability of the gel for its application in fire prevention. This paper uses a permeation device, as shown in Figure 2, to calculate the permeability.

A fixed mass of gel is poured into the device, and after 30 min, the gel mass at the outlet is weighed. Permeability is the



Figure 2. Experimental setup for penetration testing.

ratio of the gel mass at the outlet to the initial mass, as shown in eq 1.

$$P_R = \frac{m_2}{m_1} \times 100\% \quad (1)$$

where P_R refers to permeability; m_1 is the mass of the initial gel, g; and m_2 is the mass of the gel at the outlet, g.

2.3. Chemical Properties of Gels. **2.3.1. Programmed Temperature Rise Experiments.** The experimental setup comprises a self-developed programmed heating and oxidation system, as shown in Figure 3. The programmed heating system

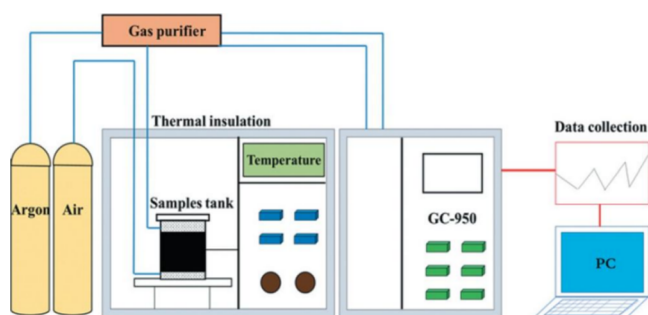


Figure 3. Programmed temperature rise oxidation system.

and gas chromatography were combined to simulate the heating and oxidation processes of coal. The release patterns of gaseous products during the heating process and other indexed parameters were recorded in real time to provide a theoretical basis for the determination of resistive properties of MMT-like multiple network composite colloids.

2.3.2. Experiments To Determine the Reactive Functional Groups. The functional groups in coal play an active role in the initiation and transfer of free radicals during the chain reaction of coal spontaneous combustion. The changes in the functional groups of coal were analyzed at a microscopic level so as to provide a theoretical support for analyzing the mechanism of fire prevention and extinguishing composite colloids. The experimental setup includes a Fourier transform infrared spectrometer, an in situ PIKE cell, a gas supply system, and a temperature control system to achieve the real-time monitoring of changes in the functional groups of the coal sample during the programmed increase of temperature. Lignite (denoted as XM) obtained from the Chinese Ximeng coal mine, which has shown self-ignition tendencies, was used in the present study. The XM raw sample was compared with the composite colloid-treated XM coal samples. KBr powder was used as the background, and the changes in the functional

groups of the coal sample during the temperature change were investigated.

2.3.3. Thermogravimetric Analysis. Coal undergoes a series of physical and chemical changes during the heating and oxidation processes, which are accompanied by changes in the mass and heat of the coal body. The thermal analysis was conducted on an STA-449-F5 instrument (NETZSCH, Bavaria, Germany). The coal sample chosen for the experiment was XM coal. The trends of heat and mass changes during the warming and oxidation processes between the multiple network gel and the composite gel acting on the coal body were compared. The mechanism of resistance of the composite gel was determined from their correlation.

2.3.4. Fire-Extinguishing Experiments. A small fire-extinguishing experiment was conducted to investigate the fire-extinguishing properties of the montmorillonite multiple network composite colloid. The apparatus used for the investigation is shown in Figure 4. A small furnace was

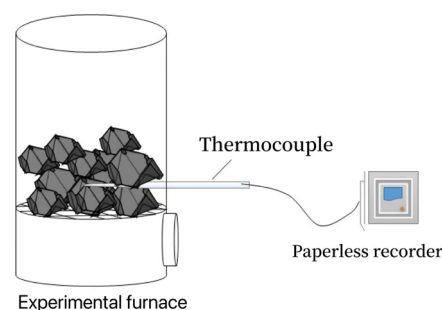


Figure 4. Schematic diagram of the setup for small fire-extinguishing experiments.

equipped with a vent at the base, a wire mesh above the base to place the coal pile, a wire mesh around the furnace body, a stretched thermocouple probe inside the coal pile through the furnace wire to measure the temperature, and a paperless recorder connected to the thermocouple to read and record the values.

3. ANALYSIS OF PHYSICAL PROPERTIES

3.1. Gel Formation Time. For this test, an L9(3⁴) orthogonal table was used to accommodate four factors, each requiring three levels, and a total of nine experiments were conducted. The gelation time experiment was repeated three times, and the average value was noted. The gelation times for the composite colloids are shown in Table 1.

The optimal amounts of MMT, PVA, and PAM and the influence of different factors and concentrations on the gelling

Table 1. Glue Formation Time

sample number	MMT concentration (A)/%	PVA concentration (B)/%	PAM concentration (C)/%	gluing time/s
1	2	2.5	0.5	558
2	2	3	1	373
3	2	3.5	1.5	121
4	3	2.5	1	412
5	3	3	1.5	283
6	3	3.5	0.5	101
7	4	2.5	1.5	310
8	4	3	0.5	185

time of the composite colloids were summarized. According to Table 1, the gel formation time of the composite colloid was most affected by the amount of PVA. The more the amount of PVA, the shorter the gel formation time of the composite colloid was. As the difference in the calculation values was extremely high, the effect of MMT content on the gelling time of the composite colloid was relatively small. When the MMT content was 2–3%, its influence on the gelling time was relatively higher. The effect of PAM content on the gelling time of the composite colloid gel was the least. In a certain range, the gelling was seen to increase with the increase in the PAM content first and then decrease.

3.2. Penetration Rate. The permeability of the composite colloid is closely related to its density or viscosity and is also influenced by the configuration and fragmentation of the coal sample. The permeability of each composite colloid was determined by varying the concentration of each base material proportionally. The experimental results are shown in Table 2.

Table 2. Results of Permeability Measurements of Composite Colloids

sample number	MMT concentration (A)/%	PVA concentration (B)/%	PAM concentration (C)/%	penetration rate/%
1	2	2.5	0.5	61.4
2	2	3	1	48.84
3	2	3.5	1.5	33.76
4	3	2.5	1	41.32
5	3	3	1.5	30.56
6	3	3.5	0.5	59.51
7	4	2.5	1.5	27.91
8	4	3	0.5	51.14
9	4	3.5	1	43.23

From the table, it is evident that the concentration of PAM had a much greater influence on the permeability of the composite colloid than the other two factors. When the concentration of PAM was 1–1.5%, it had the greatest influence on the permeability of the composite colloid. The influence of MMT content on the permeability of the composite colloid showed a stable trend. The higher the MMT content, the lower its permeability was. The PVA concentration had a minor effect on the permeability. There was an initial increase in permeability with the increase in PVA concentration, which then decreased.

The gel ratios were chosen based on the results of both the gel formation time and the permeability experiments. It was found that gel No. 5 (3% MMT + 3% PVA + 1.5% PAM) and

gel No. 7 (4% MMT + 2.5% PVA + 1.5% PAM) are more suitable for applications in mine for fire prevention. Experiments on the resistance properties were carried out using composite gels, No. 5 and No. 7.

4. CHEMICAL PERFORMANCE ANALYSES

4.1. Inhibition Rate Based on the Programmed Temperature Rise Experiment. The composite coal samples, No. 5 and No. 7, were subjected to inhibition performance experiments, and the results are shown in Figure 5. The results showed that the release of gaseous products during the rise in coal temperature could be divided into three stages: slow-release stage, rapid-release stage, and quick-release stage. The release of both CO and CO₂ decreased to different degrees in the coal samples treated with the composite gel, and the decrease was more evident in the composite gel-treated coal sample No. 7.

The slow-release stage of the gas-phase products was in the temperature range of 30–80 °C, where the coal reacted slowly with oxygen and the amount of CO and CO₂ released showed less variations. As the temperature increased, the release of gas-phase products became steady (80–120 °C). In this stage, as the coal temperature increased, heat accumulated, and the oxidation reaction accelerated, which promoted the release of CO and CO₂. As the temperature continued to increase, the complex coal–oxygen reaction intensified, and the release of gas-phase products increased exponentially. As the temperature of the coal body increased to 200 °C, the release of CO decreased by 22.31 and 41.42%, whereas the release of CO₂ decreased by 24.74 and 48.81% for the coal samples treated with composite colloids, No. 5 and No. 7, respectively. This indicated that both colloids had an inhibitory effect on coal spontaneous combustion. The increase in the MMT content, to a certain extent, improved the inhibitory effect of the colloids.

The inhibitory effect of the composite colloids can be quantified by calculating the inhibition rates from the above experimental results and using eq 2:²³

$$R = \frac{A - B}{A} \times 100 \quad (2)$$

where R is the inhibition rate, %; A is the amount of CO released from raw coal at a specific temperature, ppm; and B is the amount of CO removed from the coal treated with complex colloids at the same temperature, ppm.

As seen from Figure 6, the inhibition rates of the coal samples treated with No. 5 and No. 7 composite colloids decreased initially, then increased, and finally decreased. This

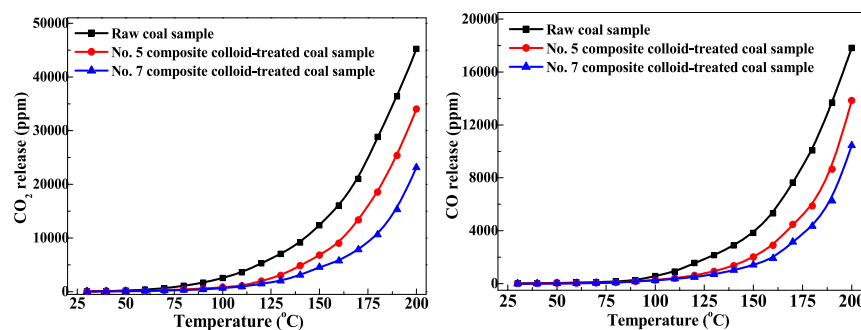


Figure 5. Trends in CO₂ and CO concentrations during coal spontaneous combustion.

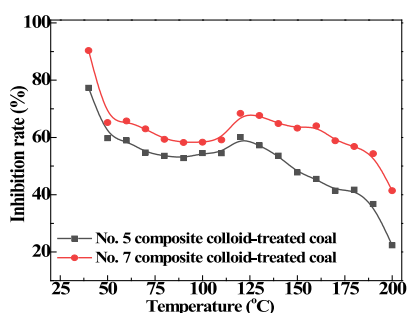


Figure 6. Trends in the inhibition rates of No. 5 and No. 7 composite colloids.

indicated that the multiple network composite colloid showed multiple inhibition effects on the coal body, with a peak at 120 °C. The performance of No. 7 composite colloid was better than that of No. 5 composite colloid.

The results of the inhibition rate showed that the release of CO and CO₂ from the two groups of coal samples treated with different ratios of colloids was significantly lower than that from raw coal during heating and oxidation. Both the composite gels had an inhibitory effect, and among them, No. 7 composite gel had a more pronounced effect on the treated coal samples.

4.2. Determination of Reactive Functional Groups.

The FTIR spectra of raw coal and No. 7 composite colloid-treated coal samples at 40, 80, 120, and 160 °C are presented in Figure 7. The figure shows the changes in the reactive functional groups of coal with temperature and the formation of microfunctional groups due to the effect of the composite colloid on the coal samples.

The broad peak at 3700–3000 cm⁻¹ was due to the hydroxyl group, whereas the peaks at 3000–2800 and 1850–1500 cm⁻¹ could be attributed to the aliphatic C–H stretching vibrations and the aromatic C=O stretching vibrations.^{24–26} Peakfit software was used to fit the different vibrational peaks of the IR spectra and to calculate the areas of stretching vibrations of peaks corresponding to the different temperatures of the active functional groups. The variations in the sizes of the hydroxyl, carbonyl, and aliphatic peaks obtained from the experiment are shown in Figure 8.

The hydroxyl contents of XM raw coal samples and the coal samples treated with composite gel decreased with the increase in temperature. The number of hydroxyl groups in the composite gel-treated coal samples was always lower than that in XM raw coal samples. The hydroxyl content of raw coal

decreased by about 30% before reaching 120 °C, while that of the coal samples treated with the gel decreased by about 12%. The reason is that PAM contains many carbonyl and amide groups, which could rapidly form intermolecular hydrogen bonds with the water molecules in coal. The free hydroxyl groups were adsorbed, and their content decreased. MMT could promote the transformation of water molecules from the free state to a stable state. This indicated that the composite colloid had good water retention properties.

The carbonyl contents in both the samples increased with the increase in temperature, but the carbonyl content of the composite colloid-treated coal samples was lower than that of the original coal samples. The amounts of carbonyl functional groups decreased by approximately 33, 29, 15, and 9% at 40, 80, 120, and 160 °C for the gel-treated XM coal samples, respectively. During the heating and oxidation phases of coal, the aliphatic and free hydroxyl groups in the coal reacted with oxygen to form various oxygen-containing functional groups, which resulted in a sharp increase in C=O compounds. The complex colloid applied to the coal body acted as a barrier against oxygen, which hindered the oxidation reaction and inhibited the oxidation of coal.

The number of aliphatic functional groups increased initially and then decreased. In the early stage, with the increase in temperature, the heat absorbed by the coal body led to the breaking of hydrocarbon molecular chains in the coal. This exposed a large number of C–H structures, in which the consumption of C–H during the oxidation of coal heating was lower than the amount produced. Hence, the C–H content increased up to 120 °C. Above 120 °C, the oxidation reaction gradually intensified, and the C–H content involved in the reaction was more than the amount produced, and its content decreased. The C–H content of the colloid-treated coal samples was always higher than that of the original coal. This indicated that the colloid reduced the rate of aliphatic oxidation reaction and effectively inhibited the thermal oxidation process of coal. With a continuous increase in temperature, there was a gradual decrease in the inhibition effect, and the aliphatic contents of the raw and colloid-treated coal samples converged gradually.

4.3. Inhibition Performance Based on TG/DSC Results. Curves for the changes in mass and heat of raw coal and colloid-treated coal samples are shown in Figure 9. The five characteristic temperatures obtained from the TG curves were: T_1 for thermal decomposition temperature, T_2 for maximum weight temperature, T_3 for ignition temperature, T_4 for the maximum point of weight loss, and T_5 for the burnout

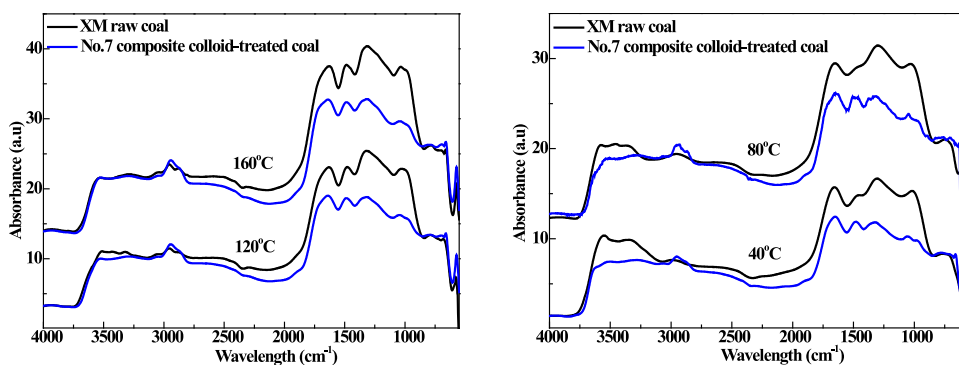


Figure 7. Comparison of the FTIR spectra of raw coal and the composite colloid-treated coal sample at different temperatures.

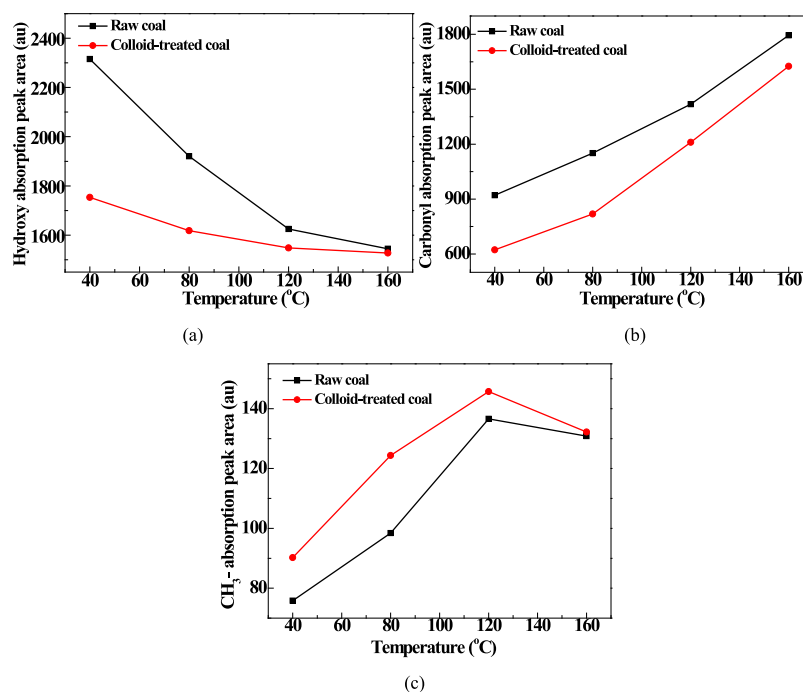


Figure 8. Changing trends of the absorption peak area for different functional groups with the increase in temperature. (a) Hydroxyl. (b) Carbonyl. (c) Aliphatic.

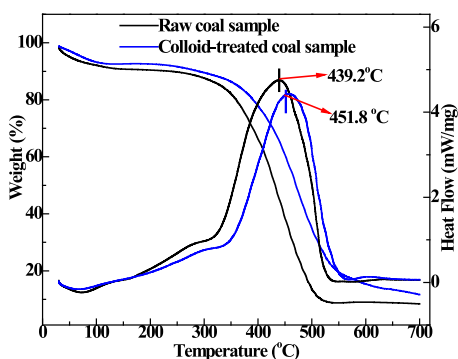


Figure 9. Effect of composite colloids on the change of weight and heat flow.

temperature. The TG curve can be divided into four stages, viz., the initial weight loss stage (T_0-T_1), the weight gain stage due to oxygen uptake (T_1-T_2), the thermal decomposition stage (T_2-T_3), the combustion stage (T_3-T_4), and the burnout stage (T_4-T_{end}).

In the initial weight loss stage, the coal samples underwent water evaporation and low-temperature pyrolysis, wherein the mass loss was rapid. The DSC curve showed an obvious peak for heat absorption. The rates of mass change of the coal sample and the composite gel-treated coal sample in this stage were about 10 and 6%, respectively. The peak area corresponding to heat absorption in raw coal was more than that of the composite gel-treated coal sample. In the weight gain stage corresponding to oxygen absorption, the oxygen chemisorbed onto coal produced hydrogen peroxide complexes. The formation rate of oxygen-containing compounds was higher than its decomposition rate, which resulted in an increase of coal mass. The TG curve showed a slight upward trend, and the DSC curve turned from negative to positive, with a gradual increase in exothermicity. At this stage, the mass

of the raw coal sample increased by 1.34%, and the mass of the composite gel-treated coal sample increased by 0.47%. This indicated that the oxygen absorption and weight gain processes of coal spontaneous combustion were hindered and the adsorption of oxygen decreased. In the thermal decomposition stage, the covalent bonds in coal were broken, which generated a large number of free radicals and gas-phase products. The mass of the coal sample decreased rapidly, and the rate of decrease gradually increased. The exothermic peak temperature T_{max} of XM coal in the DSC curve was 439.2 °C, whereas that of the composite gel-treated coal sample was pushed back by 12.6 to 451.8 °C.

The magnitude of activation energy determines the rate of oxidation of coal and is an essential parameter for analyzing the inhibition effect of the blocker at different stages. The activation energy can be calculated using the data from the TG analysis. Based on the theory of chemical reaction kinetics, the rate of oxidation of coal can be expressed by eq 3

$$\frac{da}{dt} = A \exp(-E/RT) f(a) \quad (3)$$

where a is the conversion rate during oxidative decomposition; A is the pre-factor, s^{-1} ; E is the activation energy, J/mol; T is the absolute temperature, K; R is the universal gas constant, 8.314 J/(K·mol); and $f(a)$ is a functional model reflecting the mechanism of the coal oxidation reaction.

The rate of heating $\beta = dT/dt$. Hence, eq 3 is transformed into eq 4

$$\frac{da}{f(a)} = \frac{A}{\beta} \exp(-E/RT) dT \quad (4)$$

Integrating both sides of eq 4 from 0 to a and T_0 to T provides eq 5

$$\int_0^a \frac{da}{f(a)} = g(a) = \frac{A}{\beta} \int_0^T \exp(-E/RT) dT \quad (5)$$

The approximate solution of eq 5 is sought by numerical analysis, and the Coats–Redfen integral formula is usually used in the approximate solution to obtain eq 6

$$\ln \left[\frac{g(a)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (6)$$

The kinetic model function $f(a)$ and the corresponding integration function $g(a)$ are different for different reaction mechanisms. The oxidation and combustion processes in coal are approximated as primary reactions, $g(a) = -\ln(1-a)$. By plotting $\ln \left[\frac{-\ln(1-a)}{T^2} \right]$ against $1/T$ and using linear fitting to obtain the correlation line, the kinetic parameter E can be derived from the slope of the line. Table 3 shows the activation energies of raw coal and the coal samples treated with composite gel at different stages.

Table 3. Activation Energies of Different Stages of the Coal Spontaneous Combustion Process

samples	activation energy (kJ/mol)			
	T_0 – T_1 stage	T_1 – T_2 stage	T_2 – T_3 stage	T_3 – T_4 stage
raw coal	21.87	63.36	95.41	113.30
treated coal	31.48	87.29	108.35	124.22

Results after calculation showed that the average activation energies of the gel-treated samples in the four stages of coal spontaneous combustion were 31.48, 87.29, 108.35, and 124.22 kJ/mol, respectively. They were 9.61, 23.93, 12.94, and 10.92 kJ/mol higher than the average activation energies of raw coal. These results proved that the multiple network composite gel could effectively increase the activation energy and inhibit the spontaneous combustion of coal. It is also evident from the table that the increase in the activation energy of the gel-treated coal samples in the initial weight loss stage is the highest compared to the other three stages. This indicated that the gel had a good inhibition effect throughout the heating process, and the inhibition effect in the initial weight loss stage was the best, followed by the weight gain stage with oxygen absorption.

4.4. Fire-Extinguishing Performance Analyses. The double network gel (3% PVA + 1.5% PAM) was used as a reference to investigate the fire-extinguishing performance of the composite colloid. The experimental results are shown in Figure 10. In the first 70 min, the dual network gel showed a

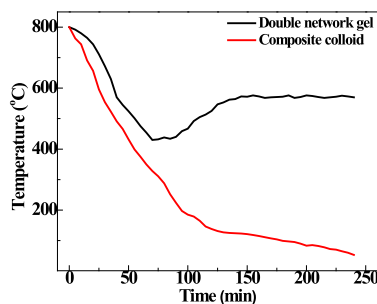


Figure 10. Temperature changes for fire-extinguishing experiments.

good fire-extinguishing performance and reduces the temperature in the fire zone from 800 to 430 °C. However, 20 min later, the temperature in the fire zone gradually raised and produced the re-ignition phenomenon due to the loss of the colloid, and the final temperature was stable at about 570 °C. From Figure 10, it can be seen that within the first 100 min, the composite colloid quickly reduced the temperature in the fire zone below 200 °C. After that, the temperature slowly dropped, and 200 min later, it dropped to below 60 °C without the phenomenon of re-ignition. Because of the properties of strong viscosity, slow flow rate, and good plugging effect, the composite colloid showed a better fire-extinguishing performance than the dual network gel during the whole fire-extinguishing process.

5. FIRE-EXTINGUISHING MECHANISM

In the multiple network composite colloid, the first network involves the covalent bonding between PVA and boric acid under alkaline conditions that initiates the further cross-linking reaction; then, the multiple cross-linked system is formed as a result of intermolecular hydrogen-bonding interactions between PAM and PVA, and the chemical cross-linking plays an important role during the intermolecular hydrogen-bonding interactions. The function of PVA chemical cross-linking is to occupy the chemical reaction sites in PVA and suppress the PVA internal cross-linking that occurred. Boric acid, as one of the most frequently used cross-linking agents, was chosen as the PVA chemical cross-linking agent. The PVA–boric acid cross-linking reaction is shown in Figure 11. The boric acid

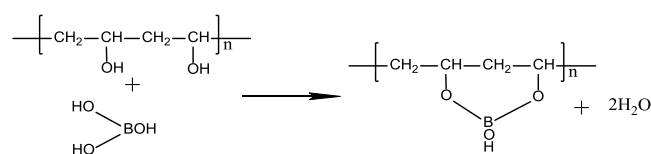


Figure 11. Schematic diagram of the PVA–boric acid cross-linking reaction.

and PVA cross-linking system can form a reversible boric acid ester bond under alkaline conditions. The preparation process is simple, economical, and practical. Moreover, the prepared gel has good elasticity and high mechanical strength.

The second network involves the cross-linking between PAM and PVA through hydrogen bonds. The large number of hydroxyl, carbonyl, and amide groups in the molecular chains of PAM and PVA can interact with water molecules forming intermolecular hydrogen bonds. At the same time, intermolecular hydrogen bonds can also be formed between the two molecules, displaying a stable three-dimensional mesh structure at a microscopic level. MMT has excellent hydrophilicity and adsorption capacity. During gel preparation, the uniform distribution of MMT within the polymer significantly improves its stability and flame retardancy. The different types of intermolecular hydrogen bonds are shown in Figure 12.

The crystal structure of MMT shows a layer of Al–O octahedron sandwiched between two layers of Si–O tetrahedra. The adjacent layers are closely connected through van der Waals and electrostatic forces, with a large number of free water molecules and cations between the layers.

The composite gel displays multiple water retention effects. The main component of the gel is water; hence, the evaporation of moisture prior to heat absorption during fire,

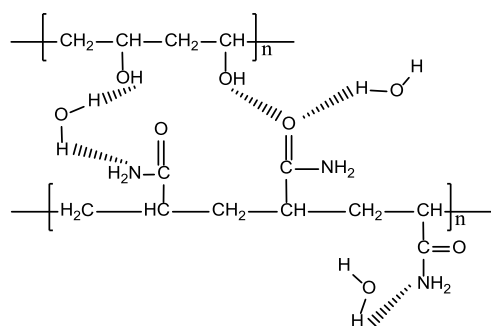
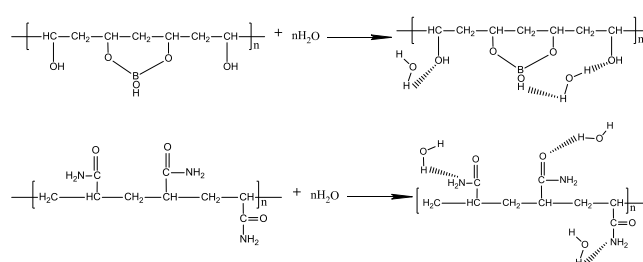


Figure 12. Different modes of intermolecular hydrogen bonding.

action of water in the coal body at a high temperature, and instant evaporation of water during heat absorption affect the fire-extinguishing mechanism in coal. The good water retention properties of the composite gel were supported by infrared spectroscopy, wherein the hydroxyl contents of the composite gel-treated coal samples were always lower than that of original coal. The hydroxyl content of original coal was decreased by about 30%, whereas that of the gel-treated coal samples was decreased by about 12%. The two reasons for this are as follows: the presence of a large number of hydrophilic groups, such as $-\text{OH}$, $-\text{COOH}$, and $-\text{COONH}_2$ in the PAM and PVA molecules of the multiple network gel, forms intermolecular hydrogen bonds with water molecules, which lead to the adsorption of free hydroxyl groups in large quantities. The three-dimensional mesh structure formed in the cross-linking process of the multiple network gel helps to lock the water molecules in the mesh pores. This weakens the mobility of water molecules, and the decomposition of crystalline water slows down. The results of TG analysis show that T_1 was shifted from 117 to 124 °C, and the exothermic peak T_{max} was shifted from 439.2 to 451.8 °C in the coal sample treated with the composite gel.

This suggests that as the temperature increases, the multiple network structure breaks down, which leads to the breaking down of hydrogen bonds and continuous release of water molecules. The multiple network structure can form stable intermolecular hydrogen bonds with water molecules, as shown in eqs 7 and 8



The composite gel helps in the isolation of oxygen and coal and prevents re-ignition of the coal body. The composite gel has a suitable viscosity and loses its fluidity at the end of the gelling time. The bonds present inside the pores of coal reduce the contact area between the coal and oxygen and isolate it from oxygen. Infrared spectroscopic analysis showed that the carbonyl content of the gel-treated coal samples was lower than that of the original coal. During the oxidation and heating of coal, the functional groups on coal react with oxygen to form various oxygen-containing functional groups, leading to an increase in the carbonyl content. The C=O-containing compounds decreased by approximately 33, 29, 15, and 9% at 40, 80, 120, and 160 °C, respectively, indicating that the composite gel had a sufficiently superior oxygen barrier capability. At the same time, MMT is highly stable at high temperatures. Even after the destruction of the multiple network structure, MMT can still adhere to the surface of the coal body and play the role of filling and plugging. On continuous heating of coal, decomposition of the MMT structure occurs, and it releases metal ions, such as Al and Si. These ions block the coal–oxygen reaction and prevent re-ignition. The process is shown in Figure 13.

6. CONCLUSIONS

In this study, a new montmorillonite-type multiple network composite gel was proposed for the prevention of coal spontaneous combustion. The optimum formulation and preparation method for the multiple network composite gel was determined by the gelling experiment and performance test. FTIR and TG/DSC analyses along with other experiments helped to test the performance of the multiple network composite gel. This composite gel was successful in reducing

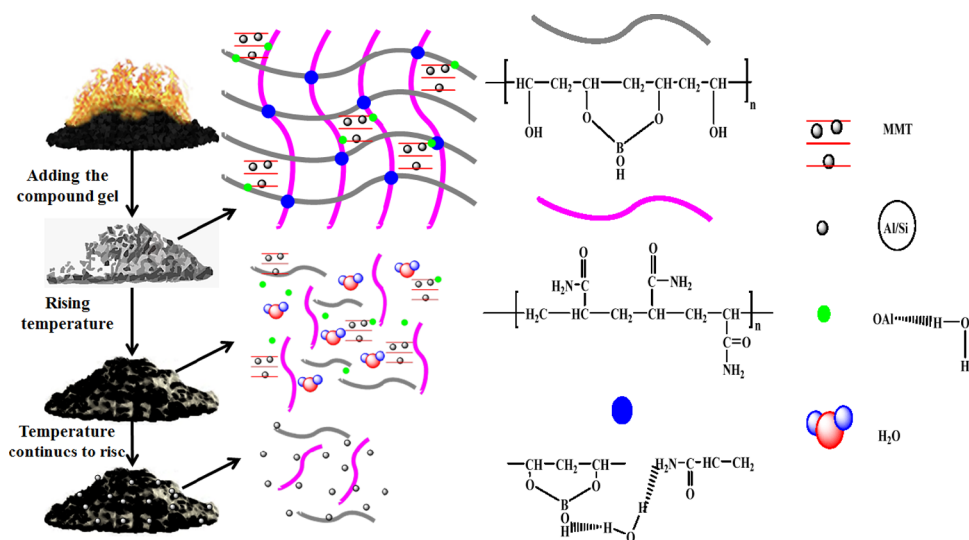


Figure 13. Composite gel fire-extinguishing mechanism.

the coal reactivity, the weight loss rate, and heat release of coal. It showed increase the critical temperature, maximum rate of temperature of weight loss, and increase in average activation energy of coal. The results showed that the multiple network composite gel could effectively inhibit the coal spontaneous combustion reaction. The flame retardancy of the composite gel was achieved due to the water absorption and expansion effects of MMT and the presence of a large number of $-OH$, $-COOH$, $-COONH_2$, and other hydrophilic groups in PVA and PAM. They form various types of hydrogen bonds with water molecules. In this way, the doubled water retention effect of the composite gel was realized. Moreover, the gel could permanently seal and fill the coal body and reduce the amount of oxygen adsorbed. Moreover, the free hydroxyl groups in coal were adsorbed by a large number of hydrophilic groups inside the organic polymer and converted into stable hydroxyl-containing compounds. Thus, the chain reaction of oxygen-containing compounds was interrupted.

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Notes

The authors declare no competing financial interest.

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